



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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(21) International Application Number: PCT/CA99/01048 (22) International Filing Date: 5 November 1999 (05.11.99) (30) Priority Data: 60/107,334 6 November 1998 (06.11.98) US (71) Applicant (for all designated States except US): THOR TECHNOLOGY CORPORATION [CA/CA]; Suite 125, 270 Yorkland Boulevard, Toronto, Ontario M2J 5C9 (CA). (72) Inventors; and (75) Inventors/Applicants (for US only): SMITH, James, W. [CA/CA]; 33 Airdrie Road, Toronto, Ontario M4G 1L8 (CA). LIANG, Zhi-Zhong [CA/CA]; 24 Chilton Hill, Richmond Hill, Ontario L4B 3B8 (CA). (74) Agents: STEWART, Michael, I. et al.; Sim & McBurney, 6th floor, 330 University Avenue, Toronto, Ontario M5G 1R7 (CA).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).  Published With international search report.	
(54) Title: BLACK LIQUOR PROCESSING			
<p style="text-align: center;">VISCOSITY VS. % SOLID + OIL</p> <p style="text-align: center;">VISCOSITY @ 80°C</p> <p style="text-align: center;">% SOLID + OIL</p> <p style="text-align: right;">         ◆ C-2 (exp)          ■ A-1          ▲ A-2          ■ C-1       </p>			
(57) Abstract			
<p>Black liquor is blended with hydrophobic hydrocarbon liquids, with or without the addition of surfactants, producing an emulsion which is readily dewatered, thereby achieving an emulsion with high solids content and of high fuel value, whilst retaining a processable viscosity at relatively low temperatures. The hydrocarbon liquid (for example, # 6 Residual Fuel or asphalt) may be of low volatility and relatively high in sulfur without adverse environmental impacts, the sulfur being captured in the recovery boiler and useful as a replacement for make up sulfur, essential in the Kraft pulping process.</p>			

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TITLE OF INVENTIONBLACK LIQUOR PROCESSINGFIELD OF INVENTION

The present invention relates to the processing of  
5 black liquor to reduce black liquor viscosity and  
achieve high solids content.

BACKGROUND TO THE INVENTION

In the Kraft process, wood or other cellulosic  
material is pulped in a white liquor comprising  
10 predominantly sodium sulfide and sodium hydroxide to  
form wood pulp. The wood pulp is separated from the  
spent pulping liquor and further processed by washing  
and optionally bleaching.

The spent pulping liquor or black liquor is  
15 subjected to a recovery and regeneration cycle for  
forming fresh pulping liquor. Such procedure generally  
involves evaporation of the black liquor, smelting the  
concentrated black liquor, forming green liquor from the  
smelt by dissolving the solid mass in water and forming  
20 white liquor from the green liquor by recausticization.

As the proportion of water decreases in the black  
liquor during evaporation, the viscosity and solids  
content of the black liquor increase. Such increase in  
viscosity tends to become exponential with solids  
25 content at solids content in excess of about 50% by  
weight. As the viscosity increases, the black liquor  
becomes more difficult to handle. In general, however,  
for the same solids content, the higher the temperature  
of the black liquor, the lower the viscosity. It would  
30 be desirable to provide a high solids content  
concentrated black liquor at lower viscosity and  
temperature to improve the processability and economics  
of recovery of the black liquor.

The relatively high viscosity of black liquor is believed to be due to the interaction of polymers, particularly hemicellulose and lignin. The hemicelluloses tend to entangle, and both hemicellulose and lignin form agglomerates which are not readily plasticized by water at solids concentrations much in excess of about 50%.

The formation of lignin agglomerates is believed to be due to four mechanisms, namely hydrogen bonding, stereoregular association, lyophobic bonding and charge transfer bonding. Such association leads to extremely high viscosity of black liquor at solids concentration in the range of 70 to 80%.

In published WO 96/26316 and corresponding U.S. Patent No. 5,705,032, assigned to the assignee hereof and the disclosure of which is incorporated herein by reference, there is described a procedure in which black liquor is subjected to high shear to cause a breakdown of macromolecular agglomerates and entanglements contained therein by shearing or milling, such as by the use of a rotor-stator combination or other equipment primarily intended to shear molecules, and provide a reduction in viscosity, which improves the processability of the black liquor and permits a higher solids content for feed to the recovery boiler.

Black liquor as formed in the Kraft process is a complex colloidal system consisting of water, organic and inorganic sulfur compounds, inorganic sodium salts, primarily in the form of carbonates and sulfides, residual caustic soda, hemicellulose and lignin. The primary lignin fragments have a molecular weight of about 10,000 with a high degree of variation, but the fragments tend to agglomerate or associate with each other, as does the hemicellulose.

It is known that shearing black liquor at relatively low shear rates reduces the viscosity reversibly by shear thinning, but the hemicellulose and lignin reassociate, leading to the same high viscosities upon ageing of the processed black liquor for an hour or two. At high shear rates in excess of 25,000 reciprocal seconds, and at solids content in excess of 50% and at temperatures in excess of about 100°C, (U. S. Patent No. 5,705,032) teaches that the reduction in viscosity due to high intensity shearing is irreversible, but solids contents in excess of about 85% to 90% are still difficult to achieve. It is believed that the shearing action promotes degradation of the hemicellulose and lignin polymers by reducing the activation energy for thermal and chemical degradation. These reactions also take place at high temperature above 180°C (U. S. Patent No. 4,929,307), but the black liquor must be held at the high temperatures for some time, and the lignin tends to produce the toxic gas dimethyl sulfide. Gagnon et al (Pulp and Paper Canada 97: 12,pT428-431, 1996) have disclosed the use of a hydrophilic additive, for example, ethylene glycol, as a replacement for the plasticizing effect of water in strong liquor. The hydrophilic agents are effective, but those available are expensive, and often have relatively low fuel value. Spontak et al (U. S. Patent No. 5,900,112) have disclosed the use of certain salts, preferably isocyanate salts, for reducing black liquor viscosity, but these salts are expensive and have no fuel value, creating an additional load on the recovery boiler.

SUMMARY OF INVENTION

In accordance with the present invention, hydrocarbon liquids, for example, fuel oil, are blended  
5 with concentrated black liquor of greater than about 50% solids, at high or low shear rates with or without the addition of surfactant(s), which may occur naturally in the black liquor or be present in the hydrocarbon liquid, the surfactant(s) reducing polymer  
10 interactions such as complex formation, re-agglomeration and re-entanglement of the polymers of black liquor.

We have now found that, by the addition of hydrophobic hydrocarbon liquids, with or without the  
15 addition of surfactants and under high or low shear conditions, such polymer interactions can be reduced, and the black liquor oil blend remains processable at significantly lower water content than is otherwise possible, without additives, increased temperatures or  
20 mechanical input of high shear energy.

The fuel oil used may be No. 6 Residual (Bunker C) fuel, or asphalt, which can contain relatively high amounts of sulfur. The sulfur presents no problem in the process, since it is captured in the recovery  
25 boiler. Another advantage of using such hydrocarbon liquids as disclosed above is their low vapor pressure. Because the price of fuel oil is relatively low, and may depend inversely, at least in part, on its sulfur content, the use of hydrocarbon liquids presents an  
30 obvious economic advantage over other additives. Moreover, the fuel value of the additives disclosed herein can be advantageously used in the production of electrical energy and of steam for the processes encountered in pulp and paper mills. The quantity of

hydrophobic hydrocarbon liquid employed is generally about 1 to 50%, preferably about 2 to about 10%.

Surfactants which may be used in the present invention may be anionic, preferably sulfonates, such as  
5 dodecyl benzene sulfonate.

Alternatively, or in addition, the surfactants may be those found in fresh or recycled lubricating oil. Such lubricating oil, and/or other petroleum derivative, such as residual fuel oil, asphalt or furnace oil, may  
10 also plasticize the black liquor polymers, leading to very high "solids" content in excess of about 75%.

Accordingly, the present invention provides a method of controlling the viscosity of black liquor from a pulping operation by subjecting the black liquor to  
15 physical conditions to effect the plasticization of black liquor by the addition of hydrophobic hydrocarbon liquids, with or without the addition of surfactants and under high or low shear blending conditions, whereby the liquor containing the hydrocarbon liquids  
20 retains a processable viscosity of under about 10,000 mPa.s at a temperature of about 80°C and significantly lower water content than is otherwise achievable.

The reduction in viscosity which is achieved herein permits further processing of the black liquor,  
25 whereby the water content of the black liquor can be reduced from, say about 35% to less than about 25%, corresponding to an increase in solids content to at least about 75%.

The surfactant(s), if required, may be an anionic  
30 surfactant, and/or those contained in lubricating oil, may be added to the black liquor prior to subjecting the black liquor to the process of blending oil or may be added to the hydrocarbon liquid prior to such blending.

Further, we have found that the treated black  
35 liquor once blended with a hydrocarbon petroleum liquid,

such as asphalt, produces a high quality fuel with relatively low viscosity and with significantly higher solids content.

The invention is particularly concerned with  
5 producing black liquor with solids concentration of at least about 75% by blending a suitable hydrocarbon liquid into black liquor in a suitable shear mill, such as a Siefer mill, wherein the initial black liquor concentration is about 40 to about 75%, and a  
10 surfactant, if necessary, is added to the black liquor before the blending process.

The quantity of surfactant employed may vary, depending on the surfactant chosen and the properties of the black liquor and hydrocarbon liquid processed and is  
15 generally from about 0.1 to about 5%.

According to one aspect of the present invention there is provided a method for improving the processability of spent pulping liquor (black liquor) and/or reducing the water content of black liquor which  
20 comprises blending the black liquor with a quantity of hydrophobic hydrocarbon liquid, thereby producing an emulsion, sufficient to effect a reduction in viscosity of the emulsion over that of the black liquor by at least about 10% at a fixed water content.

25 According to another aspect of the present invention there is provided a method of controlling the viscosity of spent pulping liquor (black liquor) from a pulping operation, which comprises blending the spent pulping liquor with a hydrophobic hydrocarbon liquid  
30 while removing water from the black liquor to provide a blend and retaining a processable viscosity of less than about 10,000 mPa.s at a temperature of less than about 80°C and significantly lower water content that is otherwise achievable.



According to yet another aspect of the present invention there is provided an emulsion comprising a spent pulping liquor (black liquor), and sufficient hydrophobic hydrocarbon liquid to effect a reduction of at least about 10% of the viscosity of the black liquor in the emulsion.

According to yet another aspect of the present invention there is provided a blend of spent pulping liquor and hydrophobic hydrocarbon liquid having a solids content of at least about 75%, a moisture content of less than about 25% and viscosity of less than about 10,000 mPa.s at a temperature less than about 80°C.

#### BRIEF DESCRIPTION OF DRAWINGS

Figure 1 is a graphical representation of viscosity vs. solid content for the experiments described in the Examples below.

#### EXAMPLES

All of the following Examples were carried out on a black liquor sample obtained from a pulp mill in the southern United States processing predominantly southern pine. The initial solids content of the black liquor was about 65%. During the processing of the liquor by blending in a #2 fuel oil, and/or by shearing at 85°C, the black liquor was not degraded by the shearing action (U. S. Patent No. 5,705,032) and water was evaporated, resulting in increasingly high solids and oil content and corresponding reduction in water content over time. Because the oil is completely combustible and has a relatively high fuel value, when used, its content may be included with black liquor solids. All samples were blended at 85°C.

Example C-1 (Control)

A sample of the black liquor was blended under  
5 high shear conditions for 45 minutes at 85°C. The  
viscosity increased with increasing solids content  
until, after 45 minutes, and at a concentration of  
71.7%, it was too high to measure at 80°C with the  
instrument available (> 15,000 mPa.s). It was not  
10 expected that shearing would have any effect on  
viscosity at the low temperature (85°C) selected for  
the experiment.

Example C-2 (Control)

15

A sample of the black liquor was blended under low  
shear conditions for 45 minutes at 85°C. The viscosity  
increased with increasing solids content until, after  
45 minutes, and at a concentration of 72.7%, it was  
20 14,600 mPa.s, or higher, the reading fluctuating  
somewhat. The results at a given solids content and  
temperature are not significantly different from those  
of Example C-1, indicating that shear rate is not a  
significant variable. This observation is illustrated  
25 in Figure 1.

Example A-1 (5% #2 fuel oil)

A sample of the black liquor was blended with the  
30 #2 fuel oil for 45 minutes at 85°C. The viscosity  
increased with increasing solids content until, after  
45 minutes, and at a concentration of 69.9% solid, or a  
combined oil + solids of 74.4, the viscosity was 7,570  
mPa.s, although fluctuating towards higher values.  
35 This Example, in contrast to Examples C-1 and C-2,

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demonstrates that a readily processable, apparently homogeneous blend can be achieved with a significant increase in solids content and decrease in water content.

5

Example A-2 (High shear, 5% #2 fuel oil, 0.5% surfactant)

A sample of the black liquor was blended with the  
10 #2 fuel oil under high shear conditions for 45 minutes at 85°C. The viscosity increased with increasing solids content until, after 45 minutes, and at a concentration of 69.9% solid, or a combined oil + solids of 74.4, the viscosity was 5,400 mPa.s, although  
15 fluctuating towards higher values. This Example, in contrast to Examples C-1 and C-2, but in concordance with Example A-1, shows that a readily processable apparently homogeneous blend can be achieved with a significant increase in solids content and decrease in  
20 water content. In contrast with Example A-1, the addition of surfactant appears to have improved the plasticizing effect of the oil additive, yielding a measurably lower viscosity.

The results of the above Examples are compiled in  
25 Tables C-1, C-2, A-1 and A-2.

**Table C-1**

BL 65% solids No Additives

- Mixed under high shear for 45 min at 85°C

	Initial	After 15 min	After 30 min	After 45 min
% moisture	35%	32%	30.1%	28.3%
% solid	65%	68%	69.6%	71.7%
Viscosity at 80°C, cP	*2800 - ↑	*3000 - ↑	*4200 - ↑	na

\*not reliable

**Table C-2**

BL 65% solids No Additives

- Mixed under low shear for 45 min at 85°C

	Initial	After 15 min	After 30 min	After 45 min
% moisture	35%	31.79%	30.20%	27.32%
% solid	65%	68.21%	69.79%	72.68%
Viscosity at 80°C, cP	2,800 - ↑	4,300 - ↑	6,400 - ↑	14,600 - ↑

**Table A-1**

BL 65% solids      Fuel Oil Additives  
Fuel Oil #2      5%

- Sample mixed under high shear at 85°C for 45 min.
- Mixer speed in the range of 2,100 to 2,600 rpm

	Before-mixing	Post-mixing
Sample weight, grams	600	530
Final % moisture, %	33.25	24.4
Final % solids, %	61.75	69.9
Viscosity at 80°C, cP	2,300 - 4600	7,750 - ↑

**Table A-2**

BL 65% solids  
Fuel Oil #2  
Surfactant

Fuel Oil + Surfactant Additives  
5%  
0.5%

- Similar mixing condition as sample "A-1"
- Surfactant: Indulin SA-L, Westvaco Chemicals.

	Before-mixing	Post-mixing
Sample weight, grams	600	529
Final % moisture, %	33.07	24.09
Final % solids, %	61.43	69.7
Viscosity at 80°C, cP	2,300 - 4,600	5,400 - ↑

The data of viscosity vs. solids content + oil  
5 (100 - % Water) are plotted in Figure 1.

This Figure shows the exponential dependence of  
viscosity on solids + oil content and the reduction in  
viscosity shown in the Tables due to the plasticizing  
effect of the hydrophobic oil. This result is  
10 unexpected, since both hemicellulose and lignin are  
highly hydrophilic. Plasticization normally requires  
the wetting of the polymer surface by the plasticizer.  
It is not expected that shear rate will have an effect  
on the viscosity of the blends, provided apparent  
15 homogeneity can be achieved. Prior art has taught that  
high shear can effect viscosity reductions of this  
magnitude only at temperatures in excess of about 100  
to 150°C.

20 SUMMARY OF DISCLOSURE

In summary of this disclosure, the present  
invention provides a novel procedure for processing  
spent pulping chemicals (black liquor) by blending the  
said black liquor with a suitable hydrophobic  
25 hydrocarbon liquid, such as recycled lubricating oil or  
fuel oil, which may permit the solid content to be  
increased and/or the processability of black liquor  
and/or the efficiency of black liquor evaporation and  
recovery furnaces to be improved, wherein re-association  
30 of degraded macromolecules is inhibited by a  
hydrocarbon/surfactant combination, said surfactant  
being naturally present in the black liquor or  
hydrocarbon liquid or added, as necessary, and said  
petroleum liquids or hydrocarbons act as plasticizers,  
35 replacing water and permitting increased solids



concentrations. The hydrocarbon liquids, such as No. 6 Residual Fuel or asphalt may contain relatively high proportions of sulfur, which in turn is captured in the recovery boiler where it is converted to a chemical form  
5 useful in the pulping process, reducing the need for the addition of make-up sulfur. Modifications are possible within the scope of the invention.

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CLAIMS

What we claim is:

1. A method for improving the processability of spent pulping liquor (black liquor) and/or reducing the water  
5 content of black liquor which comprises:  
    blending said black liquor with a quantity of hydrophobic hydrocarbon liquid, thereby producing an emulsion, sufficient to effect a reduction in viscosity of the emulsion over that of the black liquor by at  
10 least about 10% at a fixed water content.
2. The method of claim 1 wherein the water content of said black liquor emulsion is reduced by conventional means in a chemical recovery circuit whilst retaining a processable viscosity.
- 15 3. The method of claim 1 wherein the hydrophobic hydrocarbon liquid is a lubricating oil, residual fuel oil, asphalt or furnace oil.
4. A method of controlling the viscosity of spent pulping liquor (black liquor) from a pulping operation,  
20 which comprises:  
    blending said spent pulping liquor with a hydrophobic hydrocarbon liquid while the removing water from the black liquor to provide a blend and retaining a processable viscosity of less than about 10,000 mPa.s  
25 at a temperature of less than about 80°C and significantly lower water content than is otherwise achievable.
5. The method of claim 1 or 4 wherein said black liquor has a initial solids content of at least 40% and  
30 a final solids content of at least about 75%.
6. The method of claim 1 or 4 wherein the amount of hydrophobic hydrocarbon liquid is about 1 to about 50% of the blend.

7. The method of claim 1 or 4 wherein the hydrophobic hydrocarbon liquid is a lubricating oil, residual fuel oil, asphalt or furnace oil.

8. The method of claim 1 or 4 wherein the hydrophobic hydrocarbon liquid is a residual hydrocarbon fuel or asphalt containing a relatively high proportion of sulfur.

9. The method of claim 1 or 4 which is effected in the presence of a surfactant.

10. The method of claim 9 wherein the surfactant is added.

11. The method of claim 9 wherein the surfactant is naturally present in the hydrophobic hydrocarbon liquid and/or black liquor.

12. The method of claim 9 wherein said surfactant is employed in an amount of about 0.1 to about 5%.

13. An emulsion comprising a spent pulping liquor (black liquor), and a sufficient hydrophobic hydrocarbon liquid to effect a reduction of at least about 10% of the viscosity of the black liquor in the emulsion.

14. The emulsion of claim 13 wherein the hydrophobic hydrocarbon liquid is a lubricating oil, residual fuel oil, asphalt or furnace oil.

15. The emulsion of claim 13 wherein the hydrophobic hydrocarbon liquid is a residual hydrocarbon fuel or asphalt containing a relatively high proportion of sulfur.

16. A blend of spent pulping liquor and hydrophobic hydrocarbon liquid having a solids content of at least about 75%, a water content of less than about 25% and a viscosity of less than about 10,000 mPa.s at a temperature less than about 80°C.

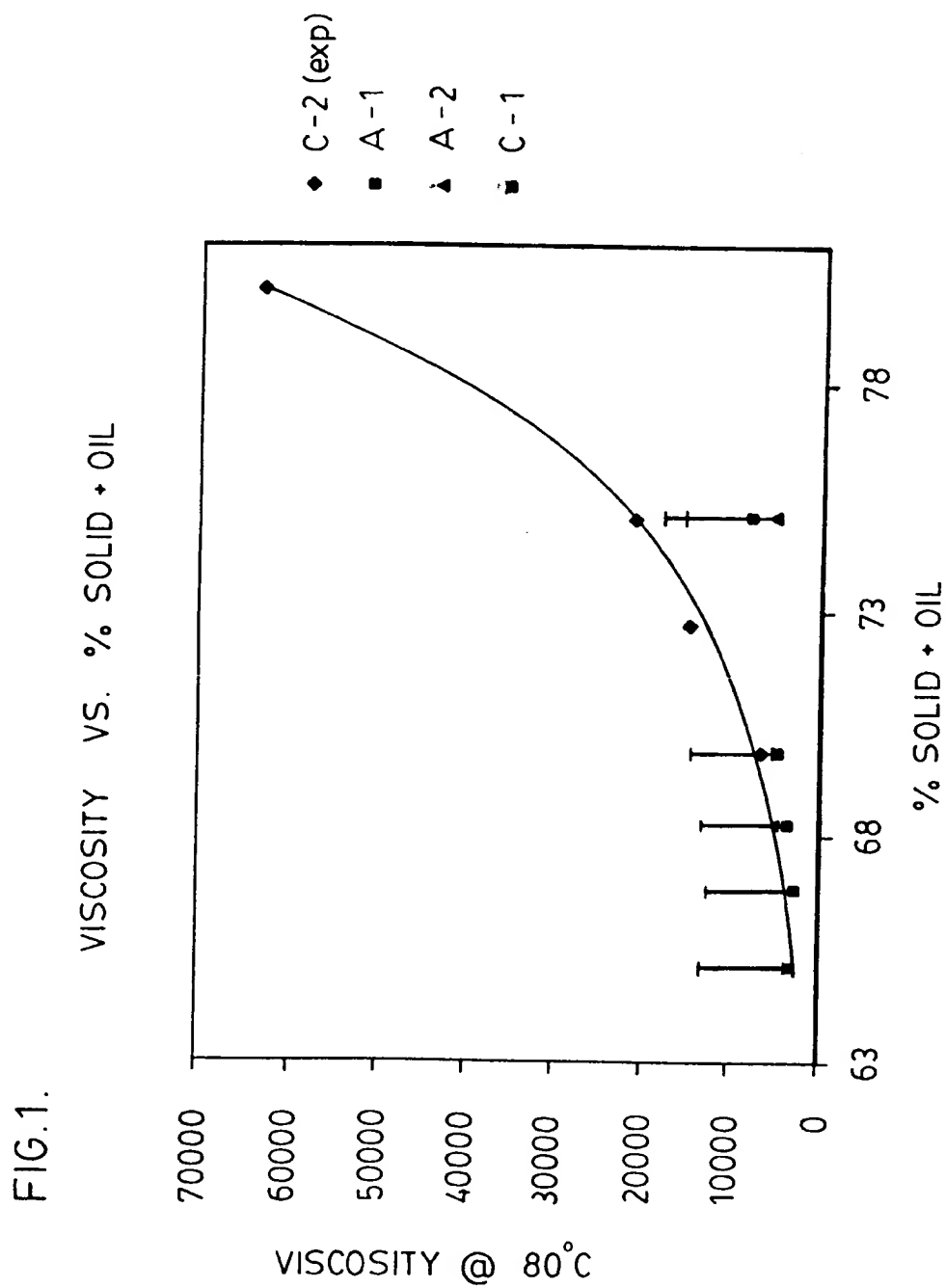
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17. A blend of claim 16 wherein the hydrophobic hydrocarbon liquid is a lubricating oil, residual fuel oil, asphalt or furnace oil.

18. A blend of claim 16 wherein the hydrophobic  
5 hydrocarbon liquid is a residual hydrocarbon fuel or asphalt containing a relatively high proportion of sulfur.

19. A blend of claim 16 further comprising a surfactant.

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# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/CA 99/01048

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 7 D21C11/00 C08L97/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 D21C C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	DATABASE WPI Section Ch, Week 198650 Derwent Publications Ltd., London, GB; Class A97, AN 1986-328971 XP002129686 & JP 61 245391 A (KATAYAMA KAGAKU KOGYO KENKYUSH), 31 October 1986 (1986-10-31) abstract	1,9,19

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

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Authorized officer

Naeslund, P

# INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/CA 99/01048

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
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